Synthesis of Cationic Pd(II) Complexes with 5-Membered Ring Chelating Iminoylcarbene Ligand and Its Catalytic Activity on Norbornene Polymerization

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Iminoyl N-heterocyclic carbine ligand with cationic allyl Pd(II) complex (**3**) was successfully synthesized by transmetallation of corresponding Ag complex with one equivalent of [Pd(allyl)(COD)]⁺SbF₆⁻. A slightly distorted square planer structure of the Pd(II) complex **3** was confirmed by single crystal X-ray diffraction analysis. The Pd(II) complex **3** is stable in air and found to show moderate activity in the polymerization of norbornene without any activator. The polynorbornene produced with Pd(II) complex **3** was obtained to be stable up to 440 °C. The ¹H and ¹³C NMR spectra of the polymer indicated addition polymerization of norbornene and the presence of the vinylene group at the end of polymer chain.

Keywords: Cationicallyl Pd(II) complex, Iminoyl N-heterocyclic, Norbornene polymerization, Catalytic activity.

INTRODUCTION

N-Heterocyclic carbenes (NHCs) and their metal complexes have been the subject of significant research interests [1-8] because of their use as active catalyst or catalyst precursors for chemical transformation in the field of organometallics. The NHC leads to organometallic complexes those are often thermodynamically robust and act as active ligands [2-5]. Almost all the transition metals have the ability to coordinate with the NHC ligand [9]. Recently NHCs-derived transition-metal complexes are being used widely for many reactions, such as olefin metathesis [10], hydrosilylation [11], C-C cross-coupling reactions [12], cycloaddition reactions [13], CO/ethylene copolymerization [14], atom transfer radical polymerization [15], but report of NHCs-derived metal complexes and their applications on olefin polymerizations is still limited [16-18].

Late-transition-metals have been developed [19-23] as catalysts for olefin polymerization. NHC-Ru complexes have been studied widely as their application in olefin metathesis catalysis [24-26] and have also been used in metathesis polymerization of different type of olefins [27,28]. However, research on the application of NHC ligands in addition polymerization of vinyl monomers is still limited. Nickel and palladium alkyls stabilized by NHC ligands undergo facile reductive elimination reactions leading to imidazolium salts, a process that may limit the applicability of such complexes to polymerization reactions [29].

It has been reported a widespread use of bidentate or polydentate ligands having strong and weak donor groups in homogeneous catalysis [30,31]. Recently there have been a few reports of metal complexes containing bidentate or poly-dentate carbene ligands and their use as catalyst precursors: such as Pd(pyimypy)₂(PF₆)₂ for copolymerization of CO/norbornene [32], *bis*(carbine)pyridine complexes of Ti and V for the polymerization of ethylene [33], picolyl-functionalized NHC carbene Ni complex for the homopolymerization of norbornene and ethylene [34], NHC carbene enolate Ni(II) complex for the polymerization of ethylene [35], tridentate salicylaldiminato NHC Ni complex for the polymerization of styrene [36]. Cationic allyl nickel complexes stabilized by a single N-heterocyclic carbene ligand and a labile aquo or acetonitrile ligand for the polymerization of 1,3-butadiene and styrene [37]. Goodall *et. al*. [38] patented the results of the polymerization of functional norbornene with monodented NHC palladium allyl complexes. Chung *et. al*. [39] reported the polymerization of functional norbornene with similar NHC palladium allyl complexes. *Bis*(aryloxide-N-heterocyclic carbene) palladium and aryl-

oxide-N-heterocyclic carbene ligated palladacycles have been reported for the homopolymerization of norbornene [40,41]. Juean *et al.* [42] reported imine-N-heterocyclic carbene palladium complexes for the homopolymerization of norbornene. The properties of the NHC ligands have been growing importance of metal complexes for olefin polymerization catalysts.

In this paper, we have synthesized and characterized a bidentate iminoyl NHC carbene ligand containing cationic allyl Pd(II) complex. Here, at first a cationic five-membered palladium complex was synthesized that exhibited good stability. Thereafter, bidentate iminoyl NHC carbene palladium complex was used as catalyst precursors for norbornene polymerization. Single crystal X-ray diffraction analysis and NMR spectra were used to characterize the structure of Pd(II) complex **3** and polynorbornene, respectively.

EXPERIMENTAL

All reactions involving organometallic compounds were carried out using the Schlenk technique unless otherwise noted. Solvents for synthesis of complex and polymerization reaction were dried according to standard procedures. Commercial grade 2,6-diisopropylaniline, benzoyl chloride, 1-methylimidazole, silver oxide, silver hexafloroantimonate, allyl palladium chloride were purchased from Aldrich. [Pd(allyl)(COD)]$^+$SbF$_6^-$ was synthesized according to the reference [42,43]. Norbornene was purified by stirring it over calcium hydride at 60 °C for 24 h and then distilled. A standard solution of norbornene in toluene (1M) was prepared and stored in a Schlenk tube.

Polymerization procedure: Polymerizations were carried out in a 100 mL glass reactor equipped with a sealed septum and a magnetic stirrer under a nitrogen atmosphere. The reactor was charged with a prescribed amount of the norbornene solution in toluene with a syringe. Solvent was added to make the total volume 30 mL. The reactor was kept in a water or oil bath at required temperature. A solution of Pd-complex (20 μmol) in methylene chloride (1 mL) and toluene (1 mL) was added to start the polymerization. The polymerization was terminated after certain time with methanol and precipitated in acidic methanol with stirring overnight. The polymers obtained were filtered, adequately washed with methanol and dried under vacuum at 60 °C for 6 h.

Analytical procedures: Molecular weight (M_n) and molecular weight distribution (M_w/M_n) of polymer were measured by GPC (Waters 150C) at 140 °C using *o*-dichlorobenzene as solvent and calibrated by polystyrene standards. ^{1}H NMR and ^{13}C NMR spectra of the copolymers were recorded at 120 °C on a JEOL GX 500 spectrometer operated at 125.65 MHz in pulse Fourier Transform mode with tetrachloroethane-d_2 as

solvent. The peak of tetrachloroethane in tetrachloroethane-d_2 (5.90 ppm for ^{1}H NMR and 74.47 ppm for ^{13}C NMR) was used as internal reference. Thermal gravimetric analysis (TGA) was studied with Seiko I & EDTA-220 under a nitrogen atmosphere up to 600 °C at heating rate of 10 °C/min. Differential Scanning Calorimetric (DSC) analysis was done on a Seiko DSC-220 under a nitrogen atmosphere from 20 to 400 °C on heating and cooling rate of 10 °C/min.

Synthesis of cationic Pd(II) complex (3): The Pd(II) complex **3** was synthesized according to **Scheme-I**. The ligand (**1**) and the silver iminoylcarbene complex (**2**) were prepared according to the reference [44]. The cationic Pd(II) complex **3** was obtained by transmetalation of the Ag carbine **2** with [Pd(allyl)(COD)]$^+$SbF$_6^-$.

In a 100 mL Schlenk tube [Pd(allyl)(COD)]$^+$SbF$_6^-$ (138 mg, 0.282 mmol) and 5 mL CH$_2$Cl$_2$ were charged under nitrogen. The tube was kept at -30 °C and a solution of Ag carbine **2** (140 mg, 0.282 mmol) in 4 mL CH$_2$Cl$_2$ was added. The mixture was stirred for 6 h at room temperature. The precipitate formed was filtered through celite and the filtrate was dried under vacuum. The white solid obtained was dissolved in CH$_2$Cl$_2$ and triturated with hexane. The mixture was kept at room temperature overnight to afford prismatic white crystal. Finally, the crystal was filtered and dried under vacuum (166 mg, 82 %). ^{1}H NMR (125 MHz, CDCl$_3$): δ 0.95 (dd, 6H, -CH-(C*H$_3$*)$_2$), 1.10 (d, 3H, -CH-C*H$_3$*), 1.21 (d, 3H, -CH-C*H$_3$*), 2.94 (sept, 1H, -C*H*-(CH$_3$)$_2$), 3.01 (d, 1H, allyl), 3.12 (sept, 1H, -C*H*-(CH$_3$)$_2$), 3.31 (d, 1H, allyl), 3.54 (d, 1H, allyl), 3.97 (s, 3H, N-C*H$_3$*), 4.18 (d, 1H, allyl), 5.51 (m, 1H, central allyl), 7.06 (m, 3H, *Ar*-di^{i}Pr), 7.16 (d, 1H, NC*H*CHN, near to N-CH$_3$), 7.31 - 7.40 (m, 5H, *Ph*), 7.49 (d, 1H, NCHC*H*N, near to imine). ^{13}C NMR (125 MHz, CDCl$_3$): δ 20.1, 20.4, 21.5, 21.8, 25.8, 26.0, 37.1, 47.1, 73.8, 117.5, 117.7, 121.6, 121.8, 122.7, 125.2, 126.6, 130.3, 136.5, 140.1, 159.4, 179.9.

RESULTS AND DISCUSSION

The cationic Pd(II) complex **3** was prepared from the transmetallation of Ag complex **2** with one equivalent of [Pd(allyl)(COD)]$^+$SbF$_6^-$. The product was obtained in high yield (82 %) and was stable in air. Colourless prismatic crystal of Pd(II) complex **3** was suitable for single crystal X-ray diffraction analysis. An ORTEP drawing of the molecular structure of complex **3** was displayed in Fig. 1. The structure verifies that the complex contains C/N chelating imino carbene ligand. Selected bond lengths and bond angles of complex **3** are given in Table-1. The central carbon of allyl was found to be disordered, where population was assumed to be 0.5 at each position. The allyl carbon *trans* to carbine shows significant length (9.5
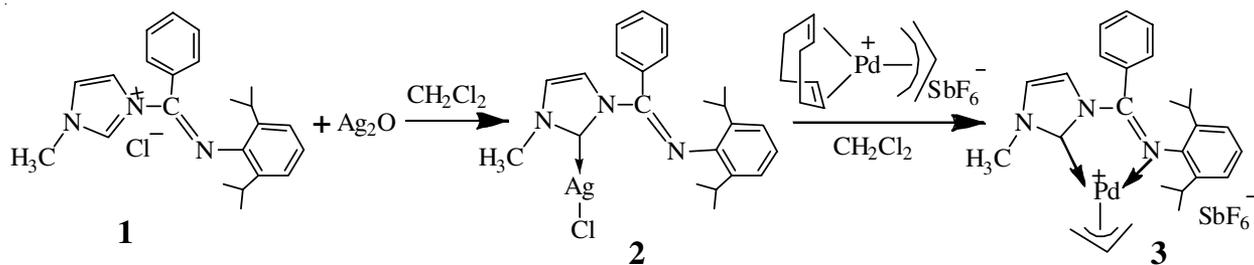
Scheme-I: Synthesis of cationic Pd(II) complex by transmetalation of Ag carbene with [Pd(allyl)(COD)]$^+$SbF$_6^-$
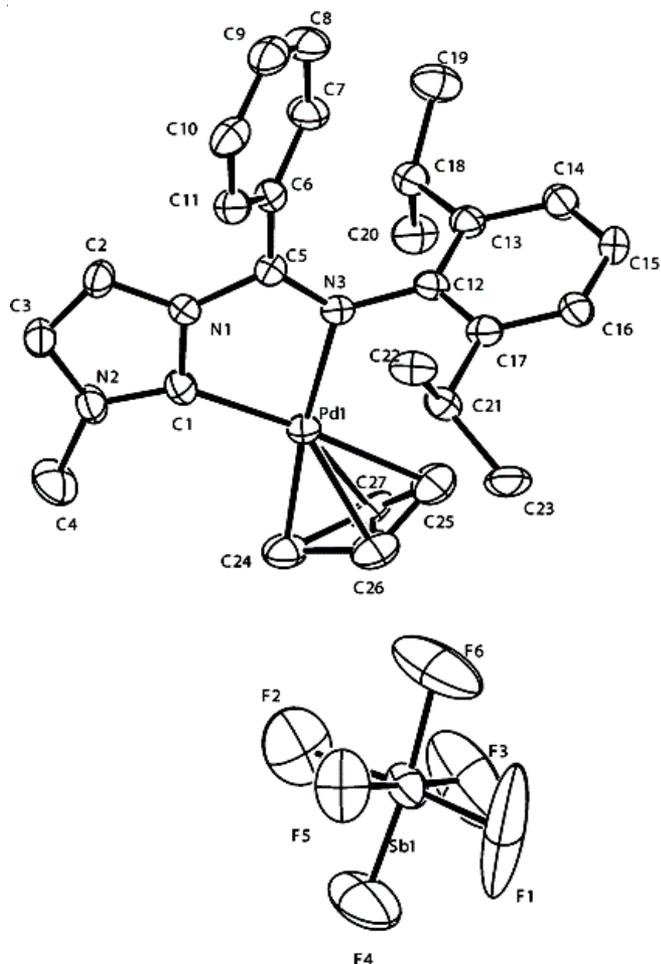
Fig. 1. ORTEP plot of Pd(II) complex (**3**). Hydrogen atoms are omitted for clarity

TABLE-1
SELECTIVE BOND LENGTHS AND
BOND ANGLES OF Pd(II)-COMPLEX **3**

Bond lengths	Å	Bond angle	°
Pd(1)-N(3)	2.136(2)	Pd(1)-C(1)-N(1)	113.05(12)
Pd(1)-C(1)	2.0125(19)	Pd(1)-C(1)-N(2)	142.89(15)
N(1)-C(1)	1.382(2)	N(3)-Pd(1)-C(1)	78.42(7)
N(2)-C(1)	1.348(2)	C(1)-Pd(1)-C(24)	107.16(8)
Pd(1)-C(24)	2.100(2)	N(3)-Pd(1)-C(25)	105.44(10)
Pd(1)-C(25)	2.195(3)		
Pd(1)-C(26)	2.185(7)		
Pd(1)-C(27)	2.136(4)		

ppm) relative to the allyl carbon *trans* to the imine. The most striking feature of the structure is that the square plane of the Pd, the imidazole ring and the 5-membered chelate ring are all coplanar. A significant ring strain on the chelate is evidenced by the fact that the two N(imidazole)-C(carbine)-Pd angles differ by 29.8° [Pd(1)-C(1)-N(2), 142.89(15)], [Pd(1)-C(1)-N(1), 113.05(12)].

Polymerization of norbornene with complex 3: Pd(II) complex **3** as a single component was evaluated as catalyst for polymerization of norbornene at 50 and 80 °C in different reaction medium. The polymerization results listed in Table-2 show that the Pd-complex **3** led to active catalyst. Temperature and solvent significantly affected the behaviour of the homopolymerization of norbornene. The activity of complex **3** was 2.75 times higher at 80 °C but the molecular weight of the polymer was about 4 times lower than the polymer obtained in same condition at 50 °C in toluene (entry 1 and 2). The catalytic activity was double and the molecular weight of the polymer obtained was increased three times, when the polymerization was carried out in a mixture of toluene and dichloromethane (1:1) at 50 °C (entry 1 and 3). At longer polymerization time (8 h), the yield was 84 % and high molecular weight polynorbornene was obtained. This result indicated that the catalyst was stable for long time during polymerization. When 10 μmol of catalyst **3** was applied, the activity was more than double compared with that of 20 μmol and the molecular weight also increased (entry 4 and 5). The narrow molecular weight distribution of all the polymers obtained (M_w/M_n = 1.48 to 2.17) indicated the single active species during polymerization.

Cationic palladium complexes [(3-Me-1-(2,6-diisopropylphenyl)iminyl-$C_3H_2N_2$)- PdMeCH$_3$CN]$^+$BAF$^-$ and [(3-(2,4,6-trimethylphenyl)-1-(2,6-diisopropylphenyl)iminyl-$C_3H_2N_2$)PdMeCH$_3$CN]$^+$BAF$^-$ were also reported [42] as active for norbornene polymerization without cocatalysts. Thermal stability of the cationic palladium complexes for norbornene polymerization was also observed.

The polynorbornene obtained was soluble in NMR solvent ($C_2D_2Cl_4$). The ^{1}H and ^{13}C NMR analyses of polynorbornene were performed in solution. The ^{1}H NMR spectrum of polynorbornene is displayed in Fig. 2. A broad signal containing four main peaks are observed around 0.99-2.30 ppm, which are assigned to methylene (CH_2) protons at 0.99-1.48 and methane (CH) protons at 1.79-2.30 ppm. Three new signals were observed at unsaturated region: two broad singlets at 5.70 and 4.70 ppm and a broad multiplet at 5.37 ppm. The relative intensities of these signals were about 1:1:1.

The two downfield peaks at 5.70 and 5.37 ppm are assignable to N–**HC**=CH–CH$_3$ proton and N–HC=**CH**–CH$_3$ proton, respectively, indicate the presence of vinylene group at the end of the polynorbornene chain. The origin of the peak at 4.70 ppm is not clear at present.

TABLE-2
HOMOPOLYMERIZATION OF NORBORNENE WITH Pd(II) COMPLEX **3**[a]

Entry	Temperature (°C)	Time (h)	Yield (g)	Activity[b]	$M_n \times 10^{-3}$ [c]	M_w/M_n [c]
1	50	4	0.34	4	21.3	2.17
2	80	4	0.87	11	5.6	1.72
3[d]	50	4	0.70	9	63.9	1.48
4[d]	50	8	2.38	15	94.8	1.80
5[e]	50	8	2.62	33	110.0	1.68

[a]Polymerization conditions; Pd = 20 μmol, N = 30 mmol, solvent = toluene, total volume = 30 mL, [b]Activity = kg(poly)·mol^{-1}(Pd)·h^{-1}, [c]Number average molecular weight and molecular weight distribution were measured by GPC analysis using polystyrene standard. [d]Solvent = (toluene 15 mL + dichloromethane 15 mL). [e]Pd = 10 μmol and Solvent = (toluene 15 mL + dichloromethane 15 mL).
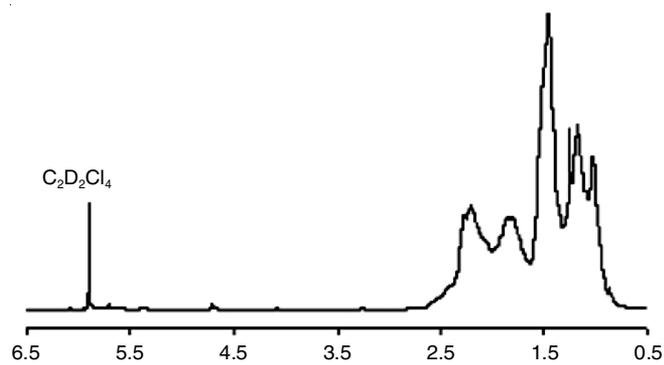
Fig. 2. ^{1}H NMR spectrum of polynorbornene obtained with **3** (entry 1)

Fig. 4. ^{13}C NMR spectrum (25-65 ppm) of polynorbornene obtained with **3** (entry 1)

In ^{13}C NMR spectrum of the polynorbornene (Fig. 3), the signals assignable to saturated carbons are appeared at 28 to 55 ppm as observed in the spectrum of the polynorbornene obtained from vinyl addition process [45,46] and five new peaks were observed at unsaturated region from 120.91 to 129.54 ppm correspond to *cis-trans* isomer of vinylene –CH=CH-CH$_3$ end group. No peak was observed at about 114 ppm or 136-138 ppm in the ^{13}C NMR spectrum that indicated the absence of vinyl (–CH=CH$_2$) end group in the polymer chain. The results suggested that the vinylene group was form by the isomerization of allyl group after the polymerization.
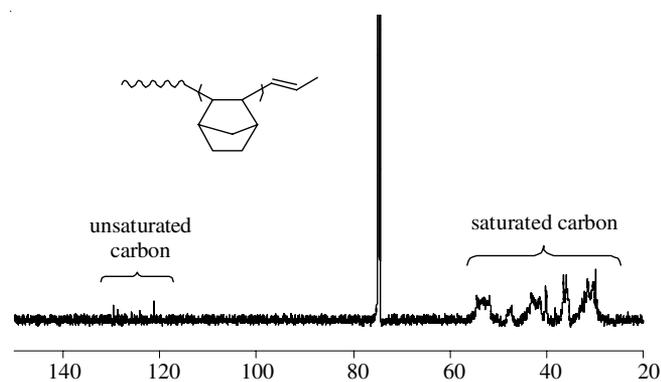

Fig. 3. ^{13}C NMR spectrum of polynorbornene obtained with Pd(II) complex **3** (entry 1)

The saturated region of the ^{13}C NMR spectrum from 25 to 65 ppm was expanded and displayed in Fig. 4. The signals of saturated carbons of polynorborne chain were observed in the range of 29.7-54.5 ppm. Each signal of saturated carbon was split into several peaks, which might come from different stereoisomers of norbornene unit in the polymer chain. The peaks were assigned as four groups by comparing peaks areas as follows: C5/C6 (29.5-33.5 ppm), C7 (35.5-38.5 ppm), C1/C2 (38.5-45 ppm and C2/C3 (47.4-54.5 ppm). Although the clear assignment of each peak was not accomplished, the three peaks of C7 carbon clearly appeared at 36.00, 36.64 and 38.29 ppm. Two peaks at 36.00 and 36.64 ppm were almost equal intensity, which suggest that the polynorbornene obtained is atactic.

The thermal property of the polynorbornene obtained from entry 5 was studied by thermogravimetric analysis. A weight loss of 4 % was recorded at 322 °C and the polynorbornene was completely decomposed at 446 °C.
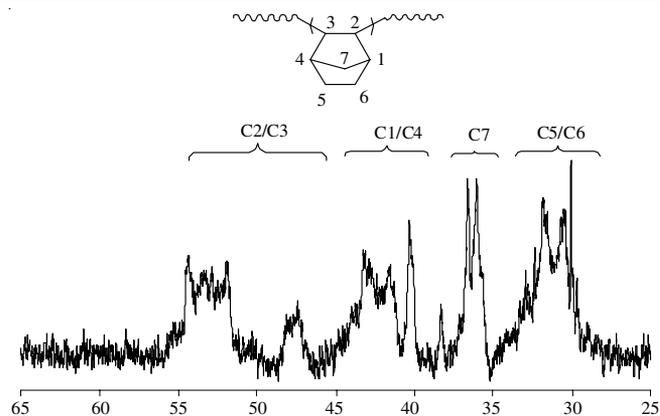
Conclusion

A cationic allyl Pd(II) complex **3** with N-heterocyclic carbene ligand was synthesized from the transmetallation of corresponding Ag complex with one equivalent of [Pd(allyl)-(COD)]$^+$SbF$_6^-$. The product was obtained in high yield (82 %) and was stable in air. The cationic palladium complex was also observed to be thermally stable as catalyst and increase the activity for long time polymerization. The molecular structure of the complex was confirmed by X-ray single crystal analysis. The NMR spectra proved the polymerization of norbornene with cationic palladium complex. The Pd(II) complex was found moderate activity for the addition polymerization of norbornene without any activator. The polynorbornene was found to be stable up to 440 °C. In polynorbornene structure, the vinylene group was obtained at the end of polymer chain.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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